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Local field dynamics in a resonant quantum tunneling system of magnetic molecules

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Abstract. We observed non-exponential relaxation for a quantum tunneling molecular magnetic system at very low temperatures and argue that it results from evolving intermolecular dipole fields. At the very beginning of the relaxation, the magnetization follows a square-root time dependence. A simple model is developed for the intermediate time range that is in good agreement with the data over 4 decades in time. Detailed numerical calculations as well as measurements are presented which indicate unusual correlation effects in these systems.

PACS. 75.45.+j Macroscopic quantum phenomena in magnetic systems – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 75.60.Ej Magnetization curves, hysteresis, Barkhausen and related effects

Recent experiments have shown evidence of quantum tunneling of the magnetization in the molecular nanomagnetic systems Fe8 [1] and Mn12ac [2,3]. General theoretical considerations for quantum tunneling of a giant spin through its anisotropy energy barrier have been proposed during the last 10 years [4]. Both Fe8 and Mn12ac can be thought of as an ensemble of identical, iso-oriented nanomagnets of net spin $S = 10$ with an Ising like anisotropy. Fe8 has the advantage in terms of tunneling measurements in that its anisotropy energy barrier is approximately 24 K compared to 63 K for Mn12ac, and its crystal symmetry affords a sizable transverse anisotropy, both of which greatly enhance tunneling effects [1,4].

At low enough temperatures (below 400 mK and approximately 1.8 K, respectively) both systems display a crossover from a thermal activated (over barrier) relaxation to a temperature independent relaxation [1,2] with a remarkable resonant structure of the relaxation time as a function of the external field [1,3]. Below these crossover temperatures and after saturation in a high field, only the $m_S = +10$ state is occupied and the only way relaxation can occur (at the first resonance field $\mathbf{B} = 0$) is by under barrier quantum tunneling from the $m_S = +10$ to the $m_S = -10$ state.

Ideally, the relaxation for non interacting, identical (giant) spins would be given by an exponential function $M(t) \propto \exp(-t/\tau)$. However, for Fe8 the data in the low temperature regime is best approximated by a stretched exponential $M(t) \propto \exp(-(t/\tau_{stretch})^{\beta})$ with $\beta \approx 0.4 - 0.5$ [1]. In this case, $\tau_{stretch}$ corresponds to an "effective" relaxation time. A stretched exponential fit is typical for spin-glasses [5] where strong interactions between spins, frustration and disorder are present, and at first seems a surprising result for Fe8. This behavior was first reported for measurements made on powdered samples of Fe8, but is also observed for measurements on single crystals presented in this article, and implies that distributions of size and orientation of particles may be ruled out as its cause. However, disorder does enter the system during the course of the relaxation: as spins flip randomly due to tunneling, their individual dipole moments give rise to a distribution of random internal fields. In addition, the surface and shape of real samples will also give rise to sizable inhomogeneous internal fields. For Mn12ac, the relaxation times in the pure quantum regime are so long that a change of only a fraction of a percent of the magnetization can be detected, even after periods of weeks, and therefore no meaningful difference can be made between single or stretched exponential behavior [2].

We present here new experimental evidence on Fe8 single crystals which shows that for "short times" (< 100 seconds) the relaxation follows a square-root time behavior. We propose a simple model which assumes a narrow tunnel splitting and an evolving Gaussian distribution of dipole fields that fits well the measured data for "intermediate times" ($< 10^5$ seconds) and gives insight to the origins of the observed stretch exponential relaxation. Finally, computer simulations of the local fields, including their dynamics are discussed in some detail for Fe8

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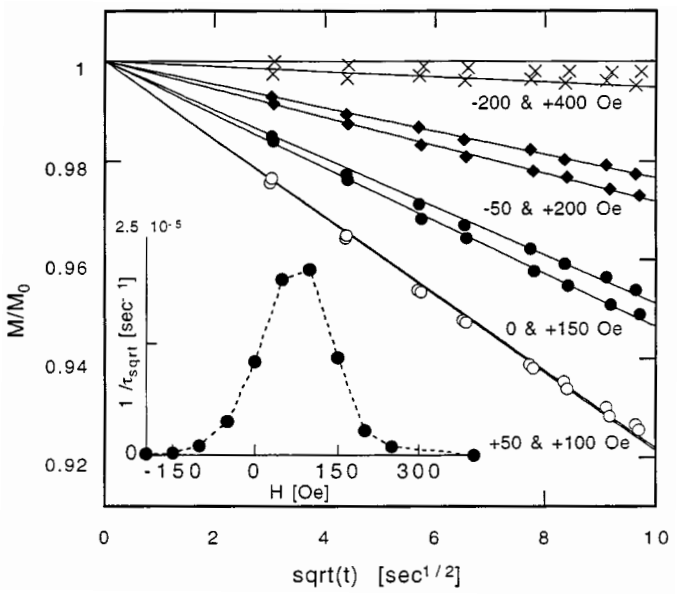

Fig. 1. The beginning 100 seconds of the relaxation of the magnetization for a single crystal of Fe8, measured at 150 mK for the indicated applied fields *versus* square-root t. (for each measurement, the sample was first saturated in a field $H > 35$ kOe). The inset shows the distribution of τ_{sqrt}^{-1} extracted from the above data as a function of field.

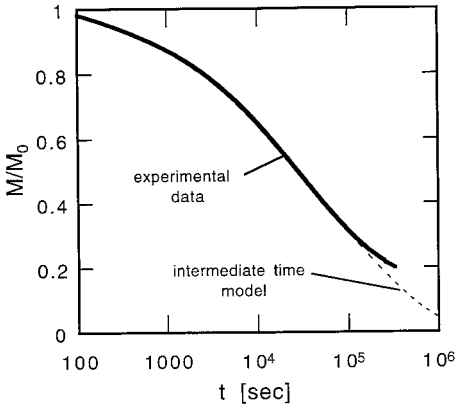

Fig. 2. Long relaxation curve measured at 150 mK and in an applied field of +80 Oe (*i.e.* at the maximum of τ_{sqrt}^{-1} *versus* H). The dashed line is the relaxation calculated by the model.

and compared to measurements, and show why at very long times the simple model and stretch exponential behavior ultimately breaks down.

Recently, Prokof'ev and Stamp predicted for the low temperature low field limit, that during the initial part of the relaxation when very few spins have turned ($1 - M/M_0 \ll 1$, with M_0 the saturation value), the magnetization should decrease as the square root of time [8,9]. Their theory is based on a narrow tunnel splitting along with an evolving Lorentzian field distribution and explicIty takes into account hyperfine fields. Figure 1 is a plot of M *versus* $\sqrt{t}$ for the beginning 100 seconds of a set of relaxation measurements taken at different values of the external applied field H_{ext}. The measurements were made at 150 mK on a roughly parallelepiped shaped single crystal of Fe8 with the easy axis along the field direction, and for each curve the sample was first saturated in a field $H > 35$ kOe. (All measurements were made using a high field low temperature SQUID magnetometer developed at the CRTBT-CNRS, Grenoble.) Although any short part of a relaxation curve may be fit to a variety of functions, an important restriction is that the extrapolation of the fits must coincide at $t = 0$. Taking this restriction into account, the best fit in the "short time" regime shows that M decays linearly on a $\sqrt{t}$-scale as $M(t) \propto 1 - \sqrt{t/\tau_{sqrt}}$ where $\tau_{sqrt}^{-1/2}$ is the slope of the linear fit as shown in the figure. In addition, τ_{sqrt}^{-1} is predicted to be proportional to the initial distribution of internal fields. The measured field dependence of τ_{sqrt}^{-1} is shown in the inset of Figure 1. The resonance is centered at about $H = +80$ Oe, and has a width of approximately 60 Oe.

Figure 2 shows a long relaxation curve for the same single crystal as Figure 1 plotted against the logarithm of the time. The measurement was made at 150 mK and in an applied field of +80 Oe, *i.e.* at the maximum of τ_{sqrt}^{-1}. For longer times we have developed a phenomenological model that fits the measured data up to 10^5 seconds. For this "intermediate time model" we assume a very narrow natural resonance width, Δ_{tunnel}, along with an *evolving* Gaussian distribution of local fields. We define $n_{\pm}(B_{||}, t)$ as the fraction of the molecular clusters with spin up/down $(+/-)$, that are in a bias field $B_{||}$ (the component of **B** along the easy axis) at time t, and normalize $n_{\pm}(B_{||}, t)$ so that the total fraction $n_{\pm}(t) = \int n_{\pm}(B_{||}, t)dB$ of clusters with spin up/down is $n_+(t) + n_-(t) = 1$. We factorize $n_{\pm}(B_{||}, t) = \rho_{dipole}(B_{||})n_{\pm}(t)$ where ρ_{dipole} explicitly describes the local field distribution. As an ansatz we use a Gaussian field distribution that is approximately valid for an increasing number of independent, randomly placed spins [10]. Thus

$$\rho_{dipole}(B_{||}) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\left(B_{||} - \mu\right)^2}{2\sigma^2}\right). \qquad (1)$$

where the variation of the width is given by $\sigma(t)^2 = \sigma_0^2 n_-(t)$, which describes the broadening of the distribution due to a growing number of turned spins. The center of the distribution shifts like $\mu(n_-(t)) = \mu_0(1 - 2n_-(t))$ due to demagnetization effects. (Experimentally we can shift the distribution by applying a small external compensation field so that the maximum is at $B_{||} = 0$). We assume a tunneling probability for a given cluster to be

$$p_{qtm}(B_{||}) = \tau_{qtm}^{-1}\delta(B_{||})\Delta_{tunnel} \qquad (2)$$

where τ_{qtm}^{-1} is the natural tunneling rate of a single isolated molecule and $\delta(B_{||})\Delta_{tunnel}$ represents a resonance centered at $B_{||} = 0$, of width Δ_{tunnel} [6]. Equation (2) states that only clusters that are within the narrow resonance can tunnel and do so with the same rate. This is in contrast to [8] where the authors take into account

hyperfine field effects which allow for a variation of the tunneling rate.

Using these definitions, we can now write a kinetic equation which describes the dynamics of the model, $\dot{n}_-(B_{||},t) = -p_{qtm}(B_{||})[n_-(B_{||},t) - n_+(B_{||},t)]$. Factoring and integrating over $B_{||}$ gives a differential equation in $n_-(t)$:

$$\dot{n}_-(t) = -\tau_{eff}^{-1}(n_-)(2n_-(t) - 1) \tag{3}$$

where

$$\tau_{eff}^{-1}(n_-) = \tau_{0\_eff}^{-1}\frac{\exp(-bn_-(t))}{\sqrt{n_-(t)}} \tag{4}$$

is proportional to the fraction of clusters in resonance. The fitting parameters are $\tau_{0\_eff}^{-1} = \tau_{qtm}^{-1}\Delta_{tunnel}/\sqrt{2\pi}\sigma_0$, and $b = \mu_0^2/2\sigma_0^2$. The differential equation (3) can be solved numerically, *e.g.* with a Runge-Kutta algorithm, and gives the relaxation of the magnetization *via* $M(t) = 1-2n_-(t)$.

The dashed line in Figure 2 is a fit to the relaxation data. Excellent agreement with the data (less than 1% error) was found over nearly 4 decades in time with the parameters $\tau_{0\_eff} = 6.6 \times 10^4$ s and $b = 7.95$. Although equation (3) still contains two fitting parameters, as does a stretched exponential, the origin of the parameters is better understood, along with their dependence on the field distribution. An estimate for $\tau_{qtm} \sim 0.1 - 1$ seconds can be obtained by using the parameter $\tau_{0\_eff}^{-1}$ and the observed values of $\sigma_0 \sim 100$ gauss and assuming a $\Delta_{tunnel} \sim 10^{-4} - 10^{-3}$ gauss [7,8]. This value is orders of magnitude faster than $\tau_{stretch}$ obtained by fitting the data to a stretch exponential [1] or τ_{sqrt} by fitting the data to a square-root law for short times. It is remarkable that the effective relaxation time of a stretched exponential or square-root fit is of the same order as τ_{0_eff}. Simply stated, the relaxation time that we measure in an experiment is $\sim \sigma_0/\Delta_{tunnel} \sim 10^5$ times slower than the tunneling rate of a single isolated molecule.

As expected, this model is not appropriate for very short times, when a Lorentzian better describes the field distribution [8,9]. For very long times, $t > 10^5$ seconds, the error of the "intermediate time model" grows rapidly and the model breaks down. A part of the problem is simply that we do not expect a relaxation to a final value of $M = 0$ because the measurements were made in a non-zero field. Adding a constant, in order to take this into account does help the fit. More interesting however is that during the course of the relaxation, the field distribution becomes increasingly distorted due to correlations which develop between spins and the assumption of a Gaussian field distribution equation (1) no longer holds.

We emphasize that the correlations are not caused by exchange interactions between clusters or by magnetic dipole *forces* which would try to align or anti-align the spins. A spin can only flip *via* tunneling if the initial and the final states are degenerate, *i.e.* the local field $\mathbf{B} = 0$, and therefore the magnetic energy of the spin does not change. Correlations come about because the weak dipole field of a spin that has tunneled can nevertheless lift the degeneracy and remove from resonance a large number of neighboring spins. These spins become effectively blocked or frozen and most wait until some new configuration of spins results in a local field close to zero. As an illustration, consider the ideal case of a spherical sample, with all spins aligned after saturation. If a small external field is applied in order to compensate for the demagnetization field, the internal field $\mathbf{B} = 0$ and all spins may be brought into resonance at once. However, as the first few spins begin to tunnel, the now uncompensated dipole fields of each one will remove from resonance all other spins within a radius r, where its dipole field $\sim 1/r^3$ is greater than Δ_{tunnel}. For $S = 10$, and a resonance width of 10^{-4} gauss, this corresponds to approximately $\sim 10^6$ spins that are pushed off resonance for each spin that tunnels! Thus very quickly most spins will be blocked and only a small fraction $\sim 10^{-6}$ of the relaxation occurs with this natural rate. Nevertheless, the relaxation does not stop completely because some spins in the vicinity of blocked regions may still be free to flip. These spins can in turn un-block spins in some overlapping volumes by compensating the internal field such that once again $\mathbf{B} < \Delta_{tunnel}$ in those regions. Then spins in these "newly liberated" volumes may flip, blocking and un-blocking other parts, and so on. For very long times, the blocked areas are so close that very few spins remain in resonance. These may still tunnel back and forth, but do not change M unless multiple flipping occurs, which we have neglected in equation (3).

To better understand the dynamics of the field distribution, we have made numerical simulations of the field distribution for different sample shapes and for different sizes up to $50 \times 50 \times 50$ cluster sites per lattice. The distribution of fields were calculated by taking into account the individual ions within each cluster, as opposed to simply replacing each cluster by a giant spin 10, which leads to spurious results. The field on an Fe^{3+} ion spin at site i (within a cluster) due to the dipole field of a given Fe^{3+} ion spin at site j outside the cluster, was calculated using the classical magneto-static result $\mathbf{B}(\mathbf{r}_{ij}) = 3\mathbf{r}_{ij}(\mathbf{m}_j\mathbf{r}_{ij})/|\mathbf{r}_{ij}|^5 - \mathbf{m}_j/|\mathbf{r}_{ij}|^3$. The $\mathbf{r}_{ij}$ are the spatial vectors pointing to the individual spins at their respective positions [11] and $\mathbf{m}_j$ the magnetic moment of the ion. We assume that the easy axis is collinear with the a-axis of the triclinic Fe8 crystal and in the following, we refer to $B_{||}(\mathbf{r}_{ij})$ as the component parallel to this axis. We define the *local bias field* at a site i as $\mathbf{B}_{||}(\mathbf{r}_i) = \sum_j \mathbf{B}_{||}(\mathbf{r}_{ij})$ where the sum j is over all the Fe^{3+} ions throughout the sample, neglecting the self-field of the ions within the cluster under consideration. We define the *weighted dipole bias field* for a cluster to be $\mathbf{B}_w = \sum_{i\in cluster} \mathbf{B}_{||}(\mathbf{r}_i)m_{S,i}/S$ where the $m_{S,i}$ corresponds to the spin state of the i-th ion within the cluster of 8 Fe^{3+} ion spins, *i.e.* for $m_S = +10$, there are 6 "up" ions $m_{S,i} = +5/2$ and 2 "down" ions $m_{S,i} = -5/2$, or *vice versa* for $m_S = -10$, where $S = |m_S| = 10$ is the total spin of the cluster [1,11].

Calculating B_w for every cluster gives the local field distribution $\rho_{dipole}(B_w)$ in the sample as shown in Figure 3. This particular calculation was made for a spherical sample of 400 Å diameter, *i.e.* a homogeneous

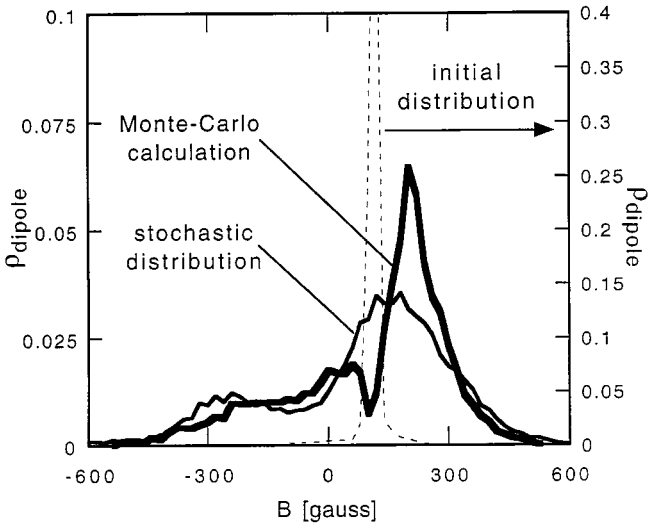

Fig. 3. Calculated local field distribution $\rho(B_w)$ for a sherical Fe8-sample of 400 Å diameter. The dashed line represents the initial saturated state, the solid and bold lines are the stochastic model and MC-simulations respectively, both for $n_- = 0.15$

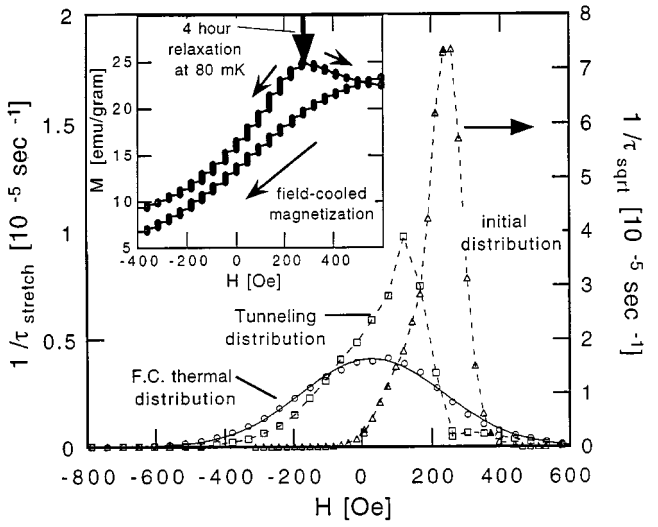

Fig. 4. Three distribution curves of $\tau_{stretch}$ and τ_{sqrt} *versus* field measured at 80 mK on a roughly spherical single crystal of Fe8. For each curve, the sample was prepared using different procedures involving the magnetic or thermal history as explained in the text.

demagnetization field. We start from the saturated state when $n_- = 0$ and all spins are aligned which can be seen as the sharp distribution centered at μ_0 (dashed line). The easy axis of the Fe8-crystal is somewhat shorter than the others, which gives rise to a positive μ_0 when the sample is saturated. This initial distribution evolves in different ways if we turn clusters stochastically, *i.e.* neglecting correlations (thin line), or if we turn according to Monte-Carlo (MC) rules (bold line) discussed below.

The stochastic simulations show a gradually broadening of the distribution $\sigma^2 = \sigma_{n0}^2 n_-$ with $\sigma_{n0} \approx 400$ gauss and the center position of the distribution μ changes linearly with n_-, thus $\mu = \mu_0^{numeric}(1-2n_-)$. The stochastic model represents a system where every spin is free to flip independent of the field it experiences, as *e.g.* for thermally activated relaxation. Thus $p_{qtm} = \tau_{TA}^{-1} = const.$ (compared to Eq. (2)) and the relaxation is single exponential as observed at high temperatures [1].

For the MC-simulations, at each time step of the calculation, the giant spin of a cluster is free to change state by tunneling with a rate τ_{qtm}^{-1}, only if the value of the local field (weighted dipole bias field) which it experiences at the time is within Δ_{tunnel} of the resonance (Eq. (2)). As usual, we have assumed that a constant external field is applied that shifts the maximum of the initial local dipole field distribution to the resonance. We have exaggerated the width of the resonance, taking $\Delta_{tunnel} = 1$ gauss. This is necessary due to the limited size of the simulations. Even so, most clusters at any given time do not fall within the resonance range and are blocked. Although the size of our simulation is limited, the MC-simulations give a stretched exponential relaxation whose actual shape is very sensitive to the chosen values of τ_{qtm} and Δ_{tunnel} and which have common features for the field distributions.

We have measured the effects of quantum tunnelling on the distribution of relaxation times as shown in Figure 4. Our numerical simulations can be qualitatively compared to these measurements, and the three curves in the figure correspond roughly to those of the simulations. All three measurements were made at 80 mK on an approximately spherical single crystal, however the sample was prepared in different ways as we shall explain below.

The sharp peaked "initial distribution" (τ_{sqrt} *versus* field) was made with the magnetization always close to the saturation value ($1 - M/M_0 \ll 1$) and was obtained by using the same procedure as that depicted in Figure 1 *i.e.* for each point the sample was first saturated, the field was then rapidly decreased to a given target field, and the relaxation of the magnetization was measured. Because the sample was close to saturation, a fit to $\sqrt{t}$ is appropriate. The peak in the distribution for this sample was approximately +230 Oe with a width of $\sim$ 120 Oe. This sharp peak corresponds roughly to the initial distribution of our computer simulations.

The other two distribution curves were made at the half demagnetized state $M \approx M_0/2$. However, there is a tremendous difference in the two distributions curves depending on how we arrive at $M_0/2$.

The "thermal distribution" was made by rapidly quenching the sample from 1 K to 80 mK in a field of 800 Oe, (*i.e.* field cooled magnetization). At 1 K and 800 Oe, M has an equilibrium value of $M \approx M_0/2$. During the rapid cooling to 80 mK ($t < 30$ seconds), the sample does not have time to change its state, either by thermal activation or tunneling (if present), and thus the thermal distribution is frozen. The distribution was then measured by sweeping the field at a fixed ramping rate, and measuring the relaxation for 20 minutes at each field as shown in the inset Figure 4. A $\tau_{stretch}$ at each field was obtained by a fit to a stretch exponential with $\beta = 1/2$.

The "tunneling distribution" was made by first saturating the sample in a high field, and then letting the sample relax in an applied field of +230 Oe (*i.e.* at the peak of the initial distribution). During this time correlations between the spins develop. After a period of 4 hours, the magnetization decreases to $M = M_0/2$, and at this point we then swept the field up to 800 Oe as shown in the inset, again measuring the relaxation for 20 minutes at each field, and obtaining $\tau_{stretch}$ from stretch exponential fits with $\beta = 1/2$. The entire procedure was repeated for the decreasing field sweep.

The difference between the thermal and quantum tunneling distributions is striking. The former is broad, and well fit by a Gaussian distribution (solid line) of width ~ 400 Oe indicating the random nature of the distribution similar to the stochastic simulations. The tunneling distribution is distorted, similar to the Monte-Carlo results, showing a depletion of the spins at the initial resonance which we believe are due the growth of correlation effects in the quantum regime. This gradual distortion results in the breakdown of the "intermediate time model", because less spins stay in resonance as predicted, and the relaxation becomes slower than the calculated curve (Fig. 2).

Finally, we point out that the field value at which we observe the fastest relaxation for the "initial distribution" is not fully understood. We noticed that its position is changing with the sample geometry (long sample: $\sim +80$ gauss, spherical sample: $\sim +230$ gauss) which should be related to the different demagnetization fields. But it can be seen from general consideration as well as from the numerical simulations that the average internal field in a saturated sample is positive and in consequence should imply a negative counterbalancing field, which is not the case.

In conclusion, we have given new evidence that intermolecular dipole fields are crucial in the understanding of the relaxation process in this molecular magnetic system.

Although the data presented were for Fe8, we believe the arguments are general, and must be taken into account for other magnetic tunneling systems as *e.g.* Mn12.

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References

1. C. Sangregorio *et al.*, PRL **78**, 4645 (1997).
2. C. Paulsen, L.G. Park, in *Quantum Tunneling of Magnetization- QTM97*, edited by L. Gunther, B. Barbara (Kluver, 1995), p. 171; C. Paulsen *et al.*, JMMM **140-144**, 379–1891 (1995).
3. M. Novak, R Sessoli, in *Quantum Tunneling of Magnetization-QTM97*, edited by L. Gunther, B. Barbara (Kluver, 1995), p. 171; J.R. Friedman *et al.* , PRL **76**, 3830 (1996); L. Thomas *et al.*, Nature **383**, 145 (1996).
4. J.L. Van Hemmen, A. Sütö, Physica B **141**, 37 (1986); M. Enz, R. Schilling, J. Phys. C **19**, 1765 (1986); E.M. Chudonovsky, L. Gunther, PRL **60**, 661 (1988); PRB **37**, 9455 (1988).
5. See *e.g.* R.V. Chamberlin *et al.*, PRL **52**, 867 (1984).
6. For convenience we express Δ_{tunnel} in units of gauss Δ'_{tunnel} [erg] $= g\mu_B S\Delta_{tunnel}$ with $g = 2$ and $S = 10$.
7. V.V. Dobrovitski, A.K. Zvezdin, Europhys. Lett. **38**, 377 (1997).
8. N.V. Prokof'ev, P.C.E. Stamp, PRL **80**, 5794 (1998).
9. N.V. Prokof'ev, P.C.E. Stamp, J. Low Temp. Phys. **104**, 143 (1996); A.L. Burin *et al.*, PRL **76**, 3040 (1996).
10. P.W. Anderson , Phys. Rev. **82**, 342 (1951); A. Abragam, A. Bleaney, *Electron Paramagnetic Resonance of Transistion Ions* (Clarendon, 1970), p. 126.
11. C. Delfs *et al.*, Inorg. **32**, 3099 (1993); K. Wieghardt *et al.*, Angew. Chem., Int. Ed. Engl. **23**, 77 (1984).